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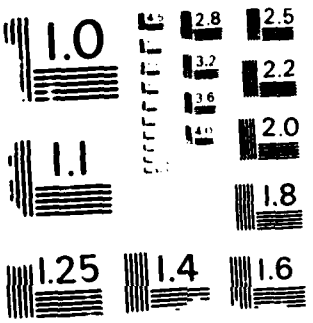
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GROWTH AND CHARACTERIZATION OF $CuGaS_2$, $CuAlS_2$ AND $CuGa_{0.9}Al_{0.1}S_2$ SINGLE CRYSTALS

BY

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ABSTRACT

In the search for suitable chalcogenides which may be used as infrared windows at 10μm, several chalcogenides of copper, gallium and aluminum have been investigated. Single crystals of $CuGaS_2$, $CuAlS_2$ and $CuGa_{0.9}Al_{0.1}S_2$ have been grown by chemical vapor transport using iodine as the transport agent. They all crystallize with the chalcopyrite structure. The energy gap, infrared transmission, stability in oxygen and microhardness have been measured for these compounds. $CuAlS_2$ has higher thermal stability and hardness than $CuGaS_2$, but its IR transmission range is smaller. The IR transmission range of the 10% solid solution lies between those of the two end members; its thermal stability and optical band gap are lower than those of both end members.

MATERIALS INDEX: Copper gallium sulfide; copper aluminum sulfide.

Introduction

Materials which are used for infrared windows at 10μm should also be thermally stable and possess considerable hardness. ZnS and ZnSe transmit in the far infrared; however, both of these compounds are relatively soft. The chalcopyrite structure is a tetrahedral structure, quite similar to the II-VI chalcogenides. It was anticipated that some of the chalcopyrites would not only transmit in the infrared, but would also be considerably harder than ZnS. Among the promising candidates which were prepared and studied were copper gallium sulfide and copper aluminum sulfide. $CuGaS_2$ and $CuAlS_2$ crystallize with the $I\text{-}III\text{-}VI_2$ tetragonal chalcopyrite structure (1-3). These compounds have been grown by chemical vapor transport and a review of many of their properties is given in the monograph by Shaw and Wernick (4). Crystals of $CuGa_{1-x}Al_xS_2$ were prepared by Inagki et al. by chemical vapor transport for photoluminescence studies (5). However, little has appeared in the literature concerning their relative hardness, thermal stability and infrared

transmission. Previous studies (6,7) of several chalcopyrites indicated that members of this group are hard, thermally stable and transmit in the far infrared. The system $CuGa_{1-x}Al_xS_2$ also crystallizes with the chalcopyrite structure and provides an opportunity to study the effect of substitution of aluminum by gallium on their properties.

Experimental

Single Crystal Growth

Single crystals of $CuGaS_2$, $CuAlS_2$, and $CuGa_{0.9}Al_{0.1}S_2$ were grown by chemical vapor transport using iodine as the transport agent. Copper (Matthey 99.999%) was reduced in an 85%Ar/15%H_2 atmosphere prior to use. Aluminum (Jarrel-Ash 99.999%) was cut into small pieces under a N_2 atmosphere prior to use. Sulfur (Gallard and Schlesinger 99.999%) was sublimed prior to use while gallium (JMC 99.999%) was used as received.

For the aluminum compounds, in order to avoid reaction with silica, stoichiometric weights of the elements with 2% extra sulfur were prepreacted in graphite tubes which were inserted in silica tubes. The tubes were then evacuated to 10^{-3} torr. The tubes were heated subsequently to 400, 500, 600, 700, 800 and 900°C and held for 12 hours at each temperature. Finally, they were heated up to 1000°C, held for 3 days, and cooled to room temperature in the furnace. The prereacted samples of $CuAlS_2$ and $CuGa_{0.9}Al_{0.1}S_2$ were then introduced into silica tubes, evacuated to 10^{-5} torr, and 5mg/cc of iodine were added. The tubes were sealed off and enclosed in a tightly wound Kanthal coil (to even out temperature gradients) and the whole assembly was placed in a three-zone furnace. The crystal growth temperature program consisted of setting the furnace to back transport mode for one day (growth zone at 1060°C and charge zone at 800°C), equilibrating the furnace to the maximum reaction temperature for three hours, and finally, cooling the central zone at 2°C/hr to the growth temperature. Optimum crystal growth occurred when the charge zone was maintained at 1000°C and the growth zone at 965°C. The transport process was carried out for two weeks, and the average crystal size was 5mm x 2mm x 1.5mm. For the growth of $CuGaS_2$, the stoichiometric weights of Cu, Ga and S were placed in an evacuated silica tube without any prereaction. The growth of crystals was achieved by the above described transport process.

Characterization

X-ray powder diffraction patterns of ground single crystals were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation (λ = 1.5405Å). For qualitative phase identification, patterns were taken with a scan rate of 1° 2θ/min, while cell parameters were determined from scans taken at 0.25° 2θ/min. Diffraction patterns were obtained over the range $12° < 2\theta < 72°$. Precise lattice parameters were obtained from these reflections using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

Optical measurements on polished single-crystal slices were performed at room temperature on a Perkin-Elmer 580 single-beam scanning infrared spectrophotometer. The measurements were performed in the transmission mode

over the range 2.5 μm - 25 μm. Transmission through the sample was normalized to the signal obtained in the absence of sample.

Transmission in the vicinity of the optical band edge was measured with an Oriel Model 1724 monochrometer, an Oriel G 772-5400 long pass filter, and a calibrated silicon diode detector. Optical band gaps were determined from the responses with and without the crystal in the beam.

The microhardness measurements (Knoop indenter) were made on crystals using a Kentron microhardness tester. The results given in Table 1 were obtained using a diamond indenter with 25 and 10 gram loads.

The stability of these compounds toward oxidation was determined by heating them in a flowing oxygen stream (65 cc/min) and monitoring the change in weight during the heating period. The decomposition temperature was determined as the temperature where the weight of the sample began to change. The results are summarized in Table 1.

TABLE 1

PROPERTIES OF $CuGaS_2$, $CuAlS_2$ AND $CuGa_{0.9}Al_{0.1}S_2$

Compound	a_o ° A	c_o ° A	Optical Energy Gap (eV)	Knoop Hardness (kg/mm^2)	Stability Limit in O_2 (°C)	Infrared Window (μm)
$CuGaS_2$	5.36(1)	10.49(1)	2.40(1)	530(100)	530	4 - 13
$CuAlS_2$	5.33(1)	10.43(1)	3.42(1)	620(100)	632	3 - 10
$CuGa_{0.9}Al_{0.1}S_2$	5.35(1)	10.48(1)	2.32(2)	540(100)	426	4 - 10.5

Results and Discussion

Single crystals of $CuGaS_2$, $CuAlS_2$ and $CuGa_{0.9}Al_{0.1}S_2$, suitable for characterization, were grown by chemical vapor transport using iodine as the transport agent. These crystals averaged 5mm x 2mm x 1.5mm. $CuAlS_2$ was blue-green and both $CuGaS_2$ and $CuGa_{0.9}Al_{0.1}S_2$ were yellow-green in color. The cell parameters of $CuAlS_2$ and $CuGaS_2$ agreed with those reported by previous investigators (1-3) and are given in Table 1, together with the cell parameters of $CuGa_{0.9}Al_{0.1}S_2$.

All three compounds crystallize with the tetragonal chalcopyrite structure. The hardness, as determined by the Knoop method, for these

compounds also is given in Table 1. It can be seen that the aluminum end member is much harder than the gallium chalcopyrite. The thermal stability, in a flowing oxygen atmosphere (see Table 1) of $CuAlS_2$ is much higher than that of $CuGaS_2$, whereas the solid solution, in which 10 atomic percent of gallium is replaced by aluminum begins to decompose at a temperature lower than both end members. The optical band gaps for the three compounds indicate that there is an initial drop in the direct band gap when 10 atomic percent of aluminum is substituted for gallium (2.40eV → 2.32eV). The compound $CuAlS_2$ has a measured direct band gap of 3.42eV. These values are also listed in Table 1. The above results resemble those found for the system $(GaP)_{1-x}(ZnSe)_x$ (7), where the measurements of the optical absorption show a sharp drop in the indirect band gap when x is increased from 0 to 0.02 followed by a gradual increase as x is increased to 0.18.

The IR transmission data summarized in Table 1 are plotted in Fig. 1. The aluminum causes a decrease in the transmission at 10 microns. Despite the increase in stability and hardness resulting from the substitution of aluminum for gallium in $CuGaS_2$, there is a marked decrease in the IR transmission range which limits the use of such materials in the far infrared.

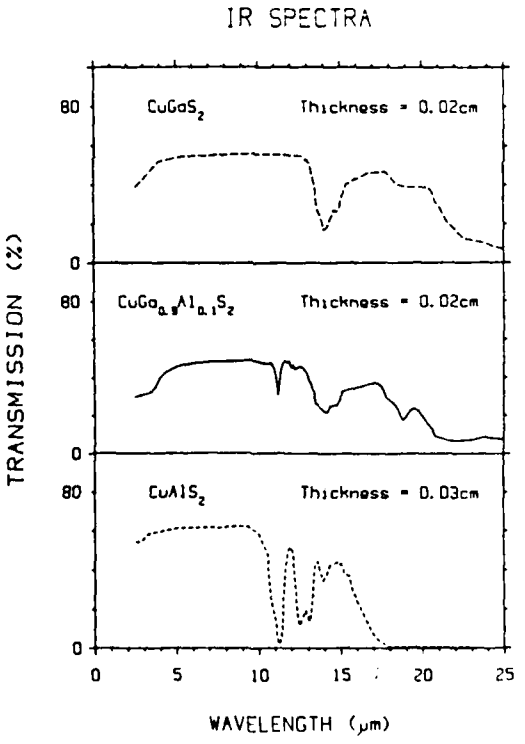

Fig. 1. Infrared Transmission of $CuGaS_2$, $CuAlS_2$ and $CuGa_{0.9}Al_{0.1}S_2$.

Conclusions

The chalcogenides $CuGaS_2$, $CuAlS_2$, as well as $CuGa_{0.9}Al_{0.1}S_2$, were prepared as single crystals and their infrared transmission, hardness and stability in oxygen as a function of temperature were measured. The $CuAlS_2$ did not transmit beyond 10μm, whereas the $CuGaS_2$ transmitted to 13μm. However the $CuAlS_2$ was considerably harder and decomposed at 632°C compared with 530°C for $CuGaS_2$. For window usage up to 10μm, $CuAlS_2$ appears to be a promising candidate. The higher transmissivity of $CuGaS_2$ is off-set by its lower hardness and thermal stability.

Acknowledgments

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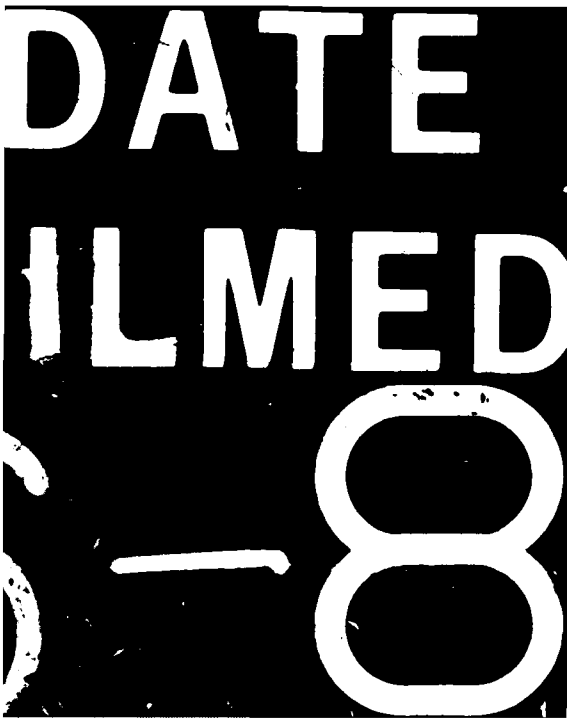
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